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VAPOR PRESSURES OF ORGANIC
EXPLOSIVE COMPOUNDS BY
AN EFFUSION METHOD

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VAPOR PRESSURES OF
ORGANIC EXPLOSIVE COMPOUNDS
BY AN EFFUSION METHOD

* * * * *

Ernest J. Kirschke

Handwritten:
Energy of Nitration
of Cellulose Nitrate
By Dr. Kirschke

Handwritten:
✓

VAPOR PRESSURES OF
ORGANIC EXPLOSIVE COMPOUNDS
BY AN EFFUSION METHOD

by

Ernest J. Kirschke
Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

United States Naval Postgraduate School
Monterey, California

1959

1962

NPS ARCHIVE

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KIRSCHKE, E

~~Thesis~~

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MASTER OF SCIENCE

IN

CHEMISTRY

from the

United States Naval Postgraduate School

ABSTRACT

The vapor pressures of trinitrotoluene and trinitroaniso^{le} were determined at temperature ranges just below their respective melting points. The vapor pressure of these substances is important in connection with calculating heats of explosion. A gas effusion technique was used in the determinations.

The writer wishes to express his appreciation for the assistance and encouragement given him by Associate Professor Richard A. Reinhardt of the U. S. Naval Postgraduate School in the pursuit of this project, and to Assistant Professor John W. Schultz also of the U. S. Naval Postgraduate School for his assistance in the construction of the apparatus.

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1. Introduction.

A knowledge of the vapor pressure of organic compounds is necessary in the evaluation of the heats of reaction of such compounds. From the vapor pressure data, the latent heat of sublimation may be determined, and this value applied to the reaction calculations. This has particular application in the determination of the heat of explosion of an organic explosive compound such as trinitrotoluene.

The objective of this project was to select a suitable method for evaluating very low vapor pressures, to fabricate the apparatus required, and finally to utilize this equipment in the determination of the vapor pressure at various temperatures for a given explosive compound.

Various techniques are available for vapor pressure studies in the expected range from one to 100 microns (1). The method attributed to the work of Knudsen (2) and based on the effusion of gases through small holes of known area was selected as applicable to this study. It has the advantage of being relatively simple in design and operation and yet sufficiently accurate to give the desired results. This method has been used by other investigators to determine the vapor pressure of trinitrotoluene (3), pentaerythritol-tetranitrate (PETN), cyclo-trimethylene-trinitramine (RDX) (4), and other nitrated aromatic compounds (5).

The materials selected for study were 2,4,6-trinitrotoluene and 2,4,6-trinitroanisole. The trinitrotoluene was selected because of the existence of conflicting data on its vapor pressure. Lange's Handbook of Chemistry (6) and The International Critical Tables (7) contain values, obtained by a McLeod Gage technique (8), which are as much as seven times higher than those found by Edwards (3) using an effusion technique. It was decided to

determine if the latter values could be reproduced. The trinitroanisole was selected as an additional test because it was expected to give values close to those of TNT. In addition, naphthalene, which has a much higher vapor pressure than either of the explosives studied, was used in the initial test to check the operation of the equipment.

The temperature range for each substance was selected so as to be below the melting point of the substance and yet high enough to give a measurable value of vapor pressure.

2. Theoretical Background.

The phenomena of effusion of a gas, upon which the Knudsen method depends, is one which deals with the flow of rarified gases through an opening in a thin diaphragm. When the linear dimensions of the opening are small in comparison to the mean free path of the molecules effusing, then simple molecular flow is said to exist. By this is meant that molecules which strike the opening, in the course of their random motion, will be transferred to the other side of the diaphragm. The rate at which they strike is dependent on the density of the gas and the velocity of the molecules.

Consider a gas enclosed in a box which is divided by a thin partition with a small hole of area A in it, as shown in figure 1.

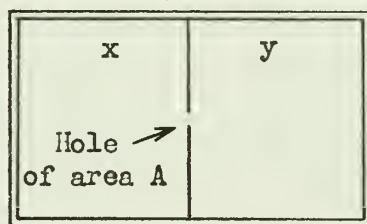


Figure 1

On side x of the partition there is a gas at pressure p_x while on the other side, y , the same gas is at pressure p_y . The temperature of both is the same; therefore, their average velocities are the same and the density of gas in either space depends only upon the pressure. If p_x is higher than p_y and the dimensions of A are less than the mean free path of the molecule at either pressure, more molecules will strike and pass through the hole from side x than from side y and there will be a net transfer of molecules through the opening.

By applying certain relationships given by the Kinetic Theory of Gases and assuming ideal gas behavior, an equation giving the amount of

material transferred may be derived. The assumption of ideality can be used in this study due to the extremely low pressures experienced. According to Loeb (9), z , the number of molecules striking a unit area per unit time in a gas space in equilibrium is given by the equation

$$z = \frac{N\bar{c}}{4} \quad (I)$$

where N is the number of molecules per unit volume of the gas space and \bar{c} is the average molecular velocity. Multiplying z by m , the mass of a molecule, gives w , the mass of the substance striking the unit area per unit time,

$$w = mz = \frac{mN\bar{c}}{4} \quad (Ia)$$

But mN is the density of the gas, d ,

$$mN = d = \frac{Mp}{RT}$$

where p is the pressure and M the molecular weight; and equation (Ia) becomes

$$w = \frac{Mp\bar{c}}{4RT} \quad (II)$$

The average velocity \bar{c} may be expressed as (9)

$$\bar{c} = \left(\sqrt{\frac{8}{3\pi}} \right) (C)$$

where C is the root mean square velocity. Given that

$$C = \sqrt{\frac{3RT}{M}}$$

then

$$z = \left(\sqrt{\frac{8}{3\pi}} \right) \left(\sqrt{\frac{3RT}{M}} \right) = \sqrt{\frac{8RT}{\pi M}}$$

and equation (II) becomes

$$w = \frac{Mp}{4RT} \sqrt{\frac{8RT}{\pi M}} = p \sqrt{\frac{M}{2\pi RT}} \quad (III)$$

where M is the molecular weight, p the pressure, and T the absolute temperature.

At the conditions existing in the partitioned box of figure 1, all of the molecules striking the opening of area A from either side will pass through. The net mass transfer per unit time G, is given by

$$G = w_x A - w_y A$$

or

$$\frac{G}{A} = w_x - w_y \quad .$$

Substituting (III) for w_x and w_y

$$\frac{G}{A} = \sqrt{\frac{M}{2\pi RT}} (p_x - p_y) \quad .$$

But G equals the mass per unit time so that the net mass of material, g, transferred from x to y through area A, during the time t, is given by

$$g = (p_x - p_y) A t \sqrt{\frac{M}{2\pi RT}} \quad (IV)$$

This equation is directly applicable to the determination of vapor pressure by the effusion method.

Consider that the substance whose vapor pressure is to be measured is placed in compartment x of the box in figure 1. If both sides of the

box are completely evacuated of other gases and the test material allowed to come to equilibrium, the pressure over the material will be its equilibrium vapor pressure at the temperature of the system. But, due to effusion, some molecules will escape from compartment x and into compartment y reducing the weight in x. If the hole in the partition through which the molecules escape is small enough, the rate of escape will not be great enough to upset the equilibrium conditions in space x. If some way is employed to remove the molecules from y as fast as they enter from x, that is p_y is kept as low as possible, very few of them will have a chance to return to x. It is then necessary to measure the loss of weight of the material in x over some measured period of time and at a fixed temperature. With the area A known and p_y negligible, or measured, equation (IV) may be rearranged and solved for p_x

$$p_x = \frac{g}{At} \sqrt{\frac{2\pi RT}{M}} + p_y \quad (V)$$

where p_x is the equilibrium vapor pressure of the material at temperature T.

3. Equipment.

In general, the equipment required for the determination of vapor pressure by Knudsen's method consists of a sealed box equipped with an orifice of known area, a vacuum flask in which the box is held during the test, a suitable method of achieving a vacuum in the flask, and a reliable constant temperature thermostat. Figure 2 is a schematic diagram of the equipment used in this project.

The sealed box as shown in figure 3 was machined from brass. Care was taken to insure that it would seal tightly when the top was in place. It measured approximately 1-1/2 inch diameter by 3/4 inch high and weighed 50 grams. A piece of brass shim stock 0.001 inch thick was soldered over a hole in the top of the box. The effusion orifice was drilled into this piece.

In selection of an orifice size, the primary consideration is that the dimensions be less than the mean free path of the molecules being studied, at the pressures experienced during the experiment. This requires estimating the vapor pressure of the substance and calculating the mean free path of the molecules at this pressure. Appendix I shows the procedure for this calculation. A second consideration is the time required for a run. A very small orifice would result in a small loss in weight per unit time. The third consideration is to avoid disturbing the equilibrium existing between the solid and vapor in the box. This will occur with too large a hole. Results of this and other experiments (3) (4) (11) indicate that an orifice whose diameter is approximately one percent of the length of the mean free path is a good choice. This matter is suggested for further study.

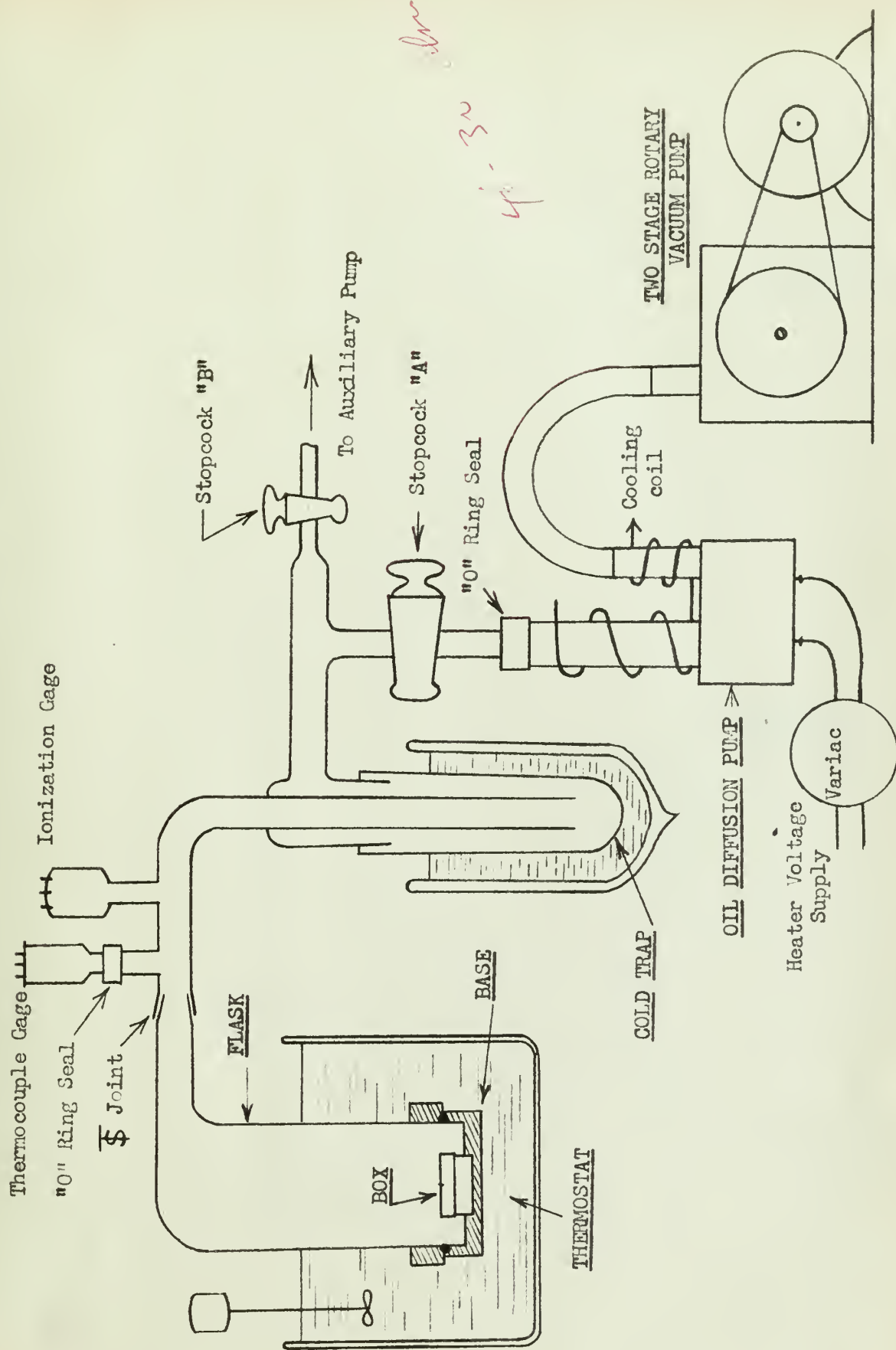
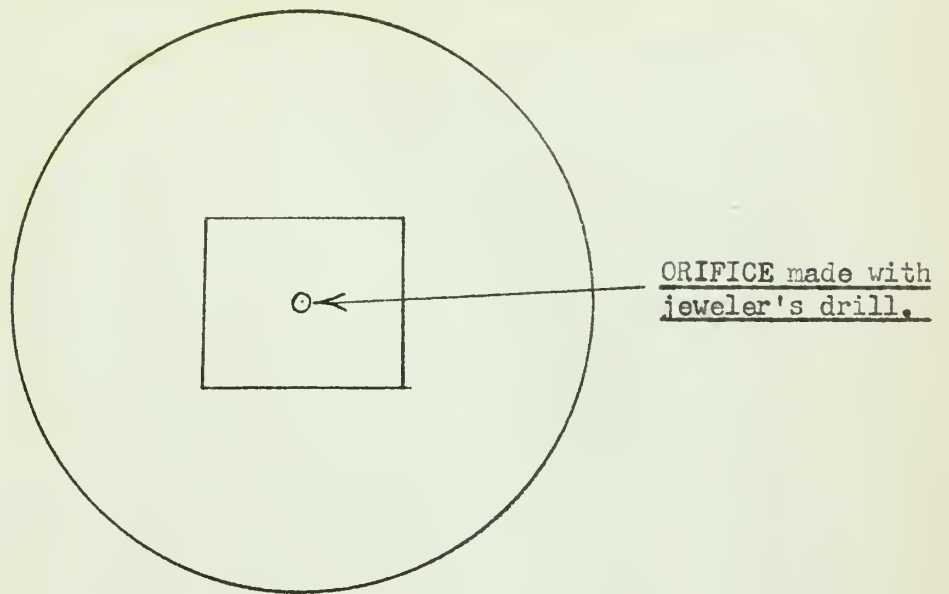
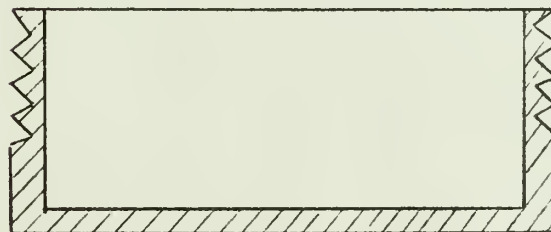
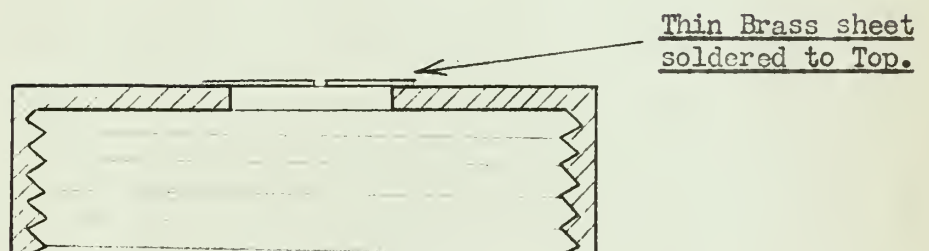


Figure 2. SCHEMATIC OF VACUUM SYSTEM





TOP



BASE

Figure 3. BOX AND ORIFICE

The design requirements for the vacuum flask and base are ease of handling and vacuum tight connection. The flask must be readily disconnected from the system and removed, and yet seal tightly to allow very high vacuums when connected. Dimensions must be large enough to allow very high pumping rates. This is accomplished by using a tube whose diameter is as large as practical and fitting it with a hand ground standard taper joint with which it connects to the system.

The purpose of the base is to seal the end of the flask, act as a receptacle for the box, and afford good heat transfer to the box. It is machined from brass and fitted with an "O" ring with which to seal it to the glass flask. Figure 4 shows both the flask and the base in an exploded view.

The basic requirement for the vacuum system is that it produce a high vacuum as fast as possible. High vacuum can be realized by keeping the system leak proof; hence the system is designed with a minimum of joints and connections. Where metal joins glass, "O" ring seals are used. These are in three places: at the base of the flask, at the thermocouple gage connection, and at the diffusion pump connection. Glass to glass joints are hand ground and sealed with Dow Corning High Vacuum Silicone Grease. The system is tested for leaks with a discharge coil. Another requirement for high vacuum is cleanliness. Appendix IV gives the cleaning and outgassing procedures recommended.

Fast pumping speeds and low resistance to flow will result in reaching high vacuum in a minimum time. The reader is referred to Yarwood (11) for a complete discussion of selection of pumping equipment. In this system a Distillation Products Company VM-20W water-cooled diffusion pump



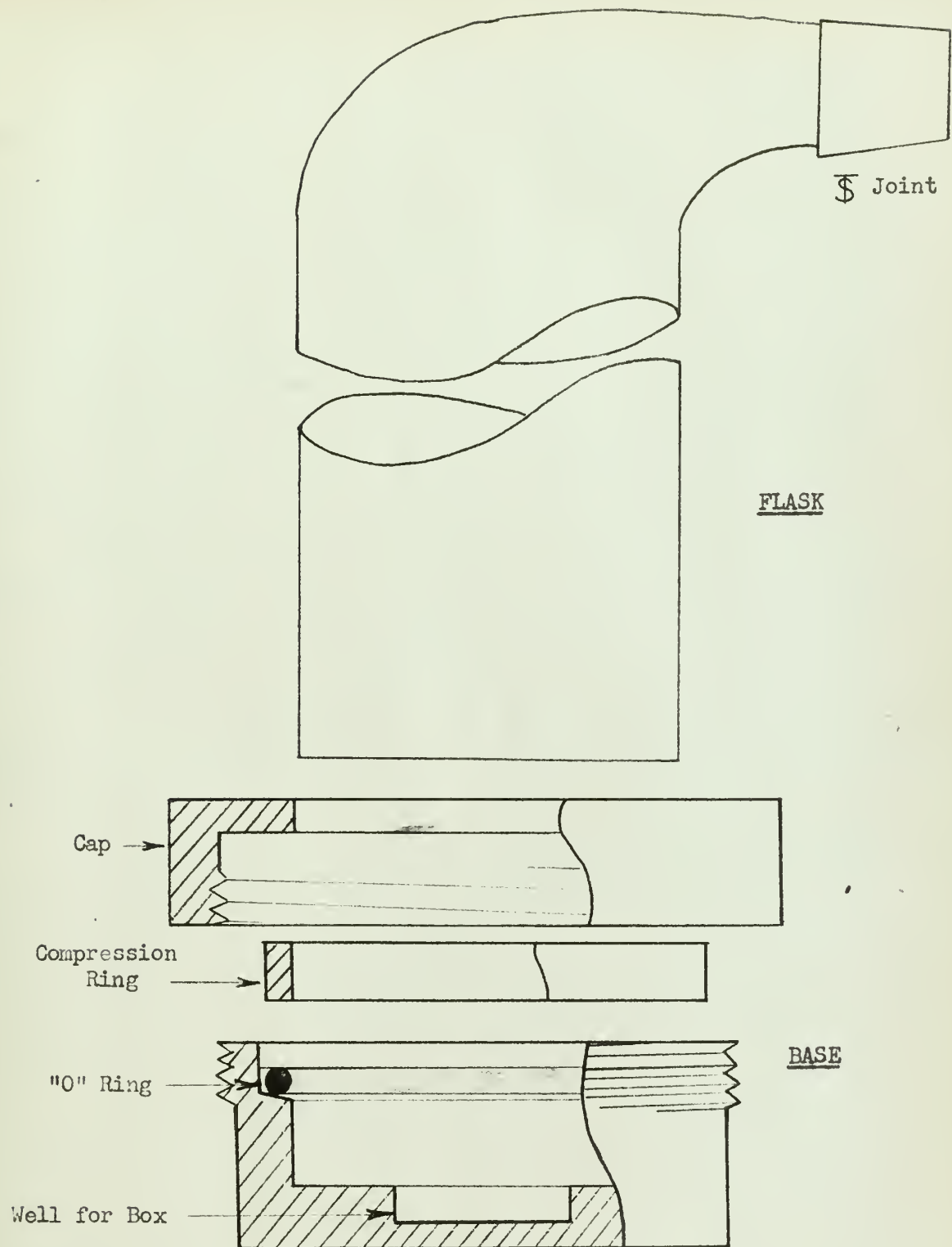


Figure 4. Flask and Base Assembly



rated at 20 liters per second is coupled with a Welch Duo-Seal 1405, two-stage rotary fore pump rated at 58.2 liters per minute. The auxiliary pump is a Cenco Hyvac, two-stage rotary pump rated at ten liters per minute. The diffusion pump heater voltage is controlled by a Variac. The pump itself is connected to the system through a large glass vacuum stopcock, A in figure 2. This allows the pump to be isolated from the system and left running when the system is opened. The fore pump is connected directly to the diffusion pump with heavy-walled rubber vacuum tubing. The auxiliary pump is connected to the system through a stopcock, B of figure 2, which also serves as a vacuum relief valve.

All parts of the system are as large in diameter and as short as possible to prevent resistance to flow and to increase pumping efficiency.

The cold trap indicated in figure 2 serves two purposes. First, it protects the pumps from harmful vapors and, second, by rapidly condensing all vapors passing through it, it increases the pumping rate. Liquid air is used in the trap to realize its maximum effectiveness.

The vacuum gages used are an NRC thermocouple gage Type 501 for pressures above one micron and an NRC ionization gage Type 507 for use at high vacuums, together with an NRC Type 710 gage control unit. The reader is referred to the instruction book accompanying these gages for further details (12).

A controlled water bath is a satisfactory constant temperature thermostat for temperatures below 80° Centigrade. Heat is supplied by means of electrical heating coils. Control is accomplished by using a mercury-to-mercury adjustable thermo regulator with an electronic

relay. Both instruments are manufactured by the Precision Scientific Corporation and when operated together have a sensitivity of 0.005 degrees. A standard laboratory mixer provides circulation of the bath liquid. For a complete discussion of temperature control the reader is referred to Chapter II of Weissberger (1).



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4. Procedure.

The material being studied was first purified, as described in Appendix II. The area of the effusion orifice was carefully measured, as described in Appendix III. The box was then charged with the material and carefully weighed. Only enough material to allow four to five successive runs was used. This amounted to about 50 or 60 milligrams and was enough to form a layer about one to two millimeters deep in the bottom of the box.

The flask and base were cleaned and baked out before each run. When necessary, the rest of the system was cleaned in accordance with the procedure in Appendix IV. A fresh change of liquid air was supplied to the cold trap for each run and by means of adjusting the position of the Dewar flask, the level of the liquid air was maintained at approximately six inches from the bottom of the trap. This insured that condensable vapors passed into the trap before condensing out and yet prevented them from being drawn through to the pumps.

After all preparations had been made, the box was placed in the brass base and that attached to the flask. The neck of the flask was stoppered and the unit placed into position in the constant temperature bath. The unit was left in this position for approximately 30 minutes to allow it to reach a steady state. At this point the temperature of the bath was very carefully checked. During this time, the fore pump was turned on and the oil diffusion pump, which was separated from the system by a stopcock, was brought up to operating temperature.

After reaching an equilibrium temperature the flask was attached to the vacuum system and, by means of the auxiliary pump, evacuation

started. When the pressure, as read by the thermocouple gage, reached 100 microns the diffusion pump was cut into the system. This caused the pressure to drop sharply and the auxiliary pump was cut out when the pressure dropped below ten microns. Below one micron the ion gage was turned on and adjusted. The system was then allowed to run for the period of the test without further adjustment. When the run was over the diffusion pump was cut out of the system and the vacuum relieved by opening stopcock B. (See figure 2.) Prior to this, the tube from stopcock B had been removed from the auxiliary pump and connected to a drying tube, so that air bled into the system would be free of moisture. The flask was disconnected from the system and taken out of the thermostat. The box was removed and placed in a desiccator to cool prior to weighing.

5. Measurements.

Timing was started when the pressure of the system reached the approximate vapor pressure of the material being studied. This usually occurred about one to one and a half minutes after starting the evacuation. The ultimate pressure was reached about three to four minutes later. This is a considerable error in short runs but becomes insignificant if times of four to five hours are used. It does indicate the necessity for rapid evacuation. Time was recorded to the nearest minute.

All weighing was done on a chain balance with weights which were calibrated against a ten gram standard weight. It was also necessary to calibrate the chain and rider of the balance. In addition, all weighings, where possible, were by difference on the chain. That is, the initial weight was so selected that the final weighing could be made with the same pan weights and rider position and by chain adjustments only. Weights were taken to the nearest tenth of a milligram.

After the thermostat had reached equilibrium, the temperature of the bath was read with a Bureau of Standards calibrated thermometer. The reading was taken with the thermometer in contact with the flask. Additional readings were made periodically during the run and just prior to the finish to insure that the thermostat had not changed. Readings were made to the nearest tenth of a degree.

The ultimate pressure of the system was read with the ionization gage. This reading was taken several times during the run and an average used in the calculation.

The vapor pressure was then calculated. Equation V on page 6 of this paper can be reduced to the following:

$$p_x = 17,143.5 \left(\frac{g}{At} \right) \left(\sqrt{\frac{T}{M}} \right) + p_y$$

where p_x and p_y are in microns; g , the grams lost by effusion; A , the area of the orifice in square centimeters; t , the time in seconds; T , the absolute temperature in degrees Kelvin; and M , the molecular weight of the substance.

6. Results.

Twelve vapor pressure determinations were made during the course of the project. One on naphthalene, five on 2,4,6-trinitrotoluene and six on 2,4,6-trinitroanisole. Table I shows the results of these runs.

The single run on naphthalene served to check the operation of the equipment. Although the orifice proved to be too large for accurate results, the value obtained was within a reasonable range of that cited in the literature. The oversized orifice was evidenced by the high rate effusion.

The determinations on trinitrotoluene were made without any apparent difficulty. The purpose of this part of the experiment was to compare the values with those obtained by Edwards (3) over the same temperature range. To do this it was first assumed that, over the small temperature range used, the vapor pressure varied with temperature according to the simple linear expression.

$$\log p = A + \frac{B}{T}$$

By applying a statistical regression analysis known as the Least Squares Estimate (13), values of the slope and intercept were estimated for each set of data. The coefficients were tested to determine if they were from the same population. The hypothesis tested was that the slope of the experimental curve was equal to that of the Edwards curve. The test statistic succeeded and the hypothesis was accepted. Details of the tests employed are long and complicated, and will not be included in this report. The reader is referred to the literature for further information. The

equations obtained by the regression analysis are as follows:

This Experiment

$$\log_{10} p \text{ (microns)} = 17.64 - \frac{5930}{T}$$

Edwards

$$\log_{10} p \text{ (microns)} = 17.00 - \frac{5697}{T}$$

Both equations are shown graphically in figure 5.

It can be stated with a high degree of confidence that this part of the project succeeded in its objective.

The second part of the project, the determination of a vapor pressure-temperature curve for crystalline trinitroanisole, was limited due to the low melting point of the material. At a temperature below its observed melting point (68.4°C) the vapor pressures of trinitroanisole drop below one micron, and the equipment was not intended for measuring pressures below this value. This situation could not be positively determined until after a determination had been made. Values for TNT at these temperatures are in a measurable range and it was because of its similiarity with TNT that trinitroanisole was selected. Six determinations were made and the high variation as compared to the determinations made on TNT points out the limitation of the equipment at pressures below one micron. In this test a three degree temperature range was used and the assumption of a simple linear relationship is valid. The same regression analysis as in the preceding test was applied to the data and the following equation resulted:

$$\log_{10} p \text{ (microns)} = 15.83 - \frac{5,391}{T}$$

Figure 6 is a graphical representation of the data with this line super-

imposed. It will be noted that although the value for the slope compares closely with those found for TNT, the value of the intercept accounts for the lower values of vapor pressures.

The reader is cautioned that the values given by these equations are for the best estimate of a straight line defined by the experimental data and are limited by the accuracy of the data.

Assuming that the Clausius-Clapeyron equation is applicable and that the heat of sublimation is constant over the temperature range studied, the heat of sublimation for the materials tested may be estimated from the straight line relationships defined above. The values so determined are as follows:

2,4,6-Trinitrotoluene	27.1 Kcal/mole
2,4,6-Trinitroanisole	24.6 Kcal/mole

The value for TNT given by Edwards (3) over the entire temperature range of his investigation is 28.3 Kcal/mole. However the value calculated from his data over the same range used in this experiment is 26.1 Kcal/mole.

<u>Temp.</u> <u>°C</u>	<u>Time-</u> <u>Sec.</u>	<u>Wt. Loss-</u> <u>GMS.</u>	<u>Orifice Area-</u> <u>CM²</u>	<u>P_x - P_y</u>	<u>P_y</u>	<u>P_x</u> <u>Microns</u>
<u>Naphthalene</u>						
32.0	7800	0.0592	6.69 x 10 ⁻⁴	300	1.0	299
<u>2,4,6-Trinitrotoluene</u>						
70.0	14760	0.0081	5.12 x 10 ⁻³	2.26	0.14	2.40
70.0	15000	0.0077	"	2.11	0.08	2.19
70.0	15360	0.0078	"	2.09	0.07	2.16
78.5	10200	0.0142	"	5.80	0.08	5.88
77.5	12000	0.0152	"	5.27	0.09	5.36
<u>2,4,6-Trinitroanisole</u>						
65.0	14400	0.0027	5.12 x 10 ⁻³	0.74	0.04	0.78
65.0	18600	0.0032	5.40 x 10 ⁻³	0.64	0.04	0.68
65.0	28800	0.0061	5.12 x 10 ⁻³	0.83	0.04	0.87
66.5	36000	0.0076	"	0.83	0.05	0.88
67.9	19800	0.0119	11.20 x 10 ⁻³	1.09	0.05	1.14
67.9	18000	0.0093	"	0.94	0.04	0.98

Table 1 - Tabulated Data and Calculated Values of Vapor Pressure P_x

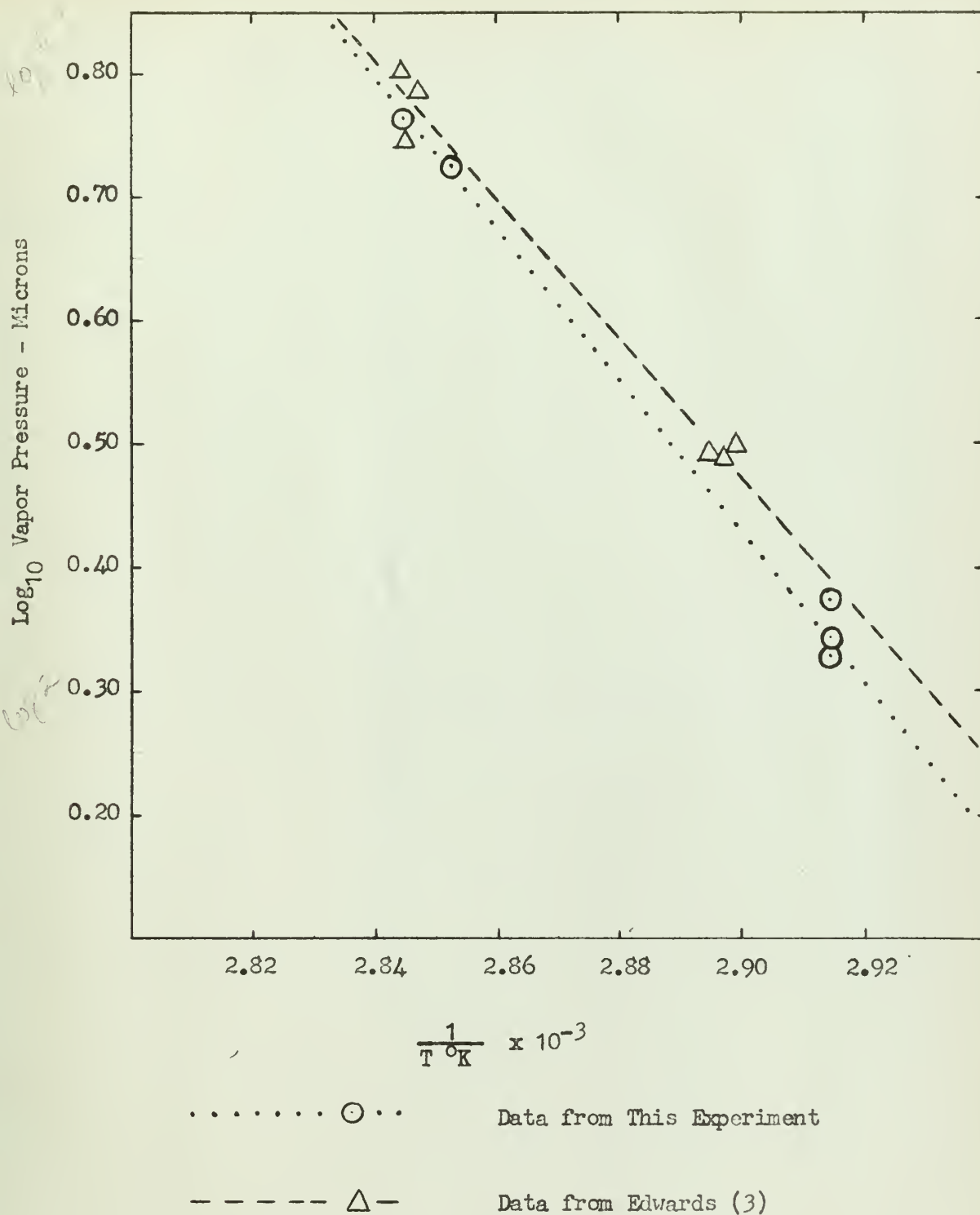


Figure 5. 2,4,6 - Trinitrotoluene

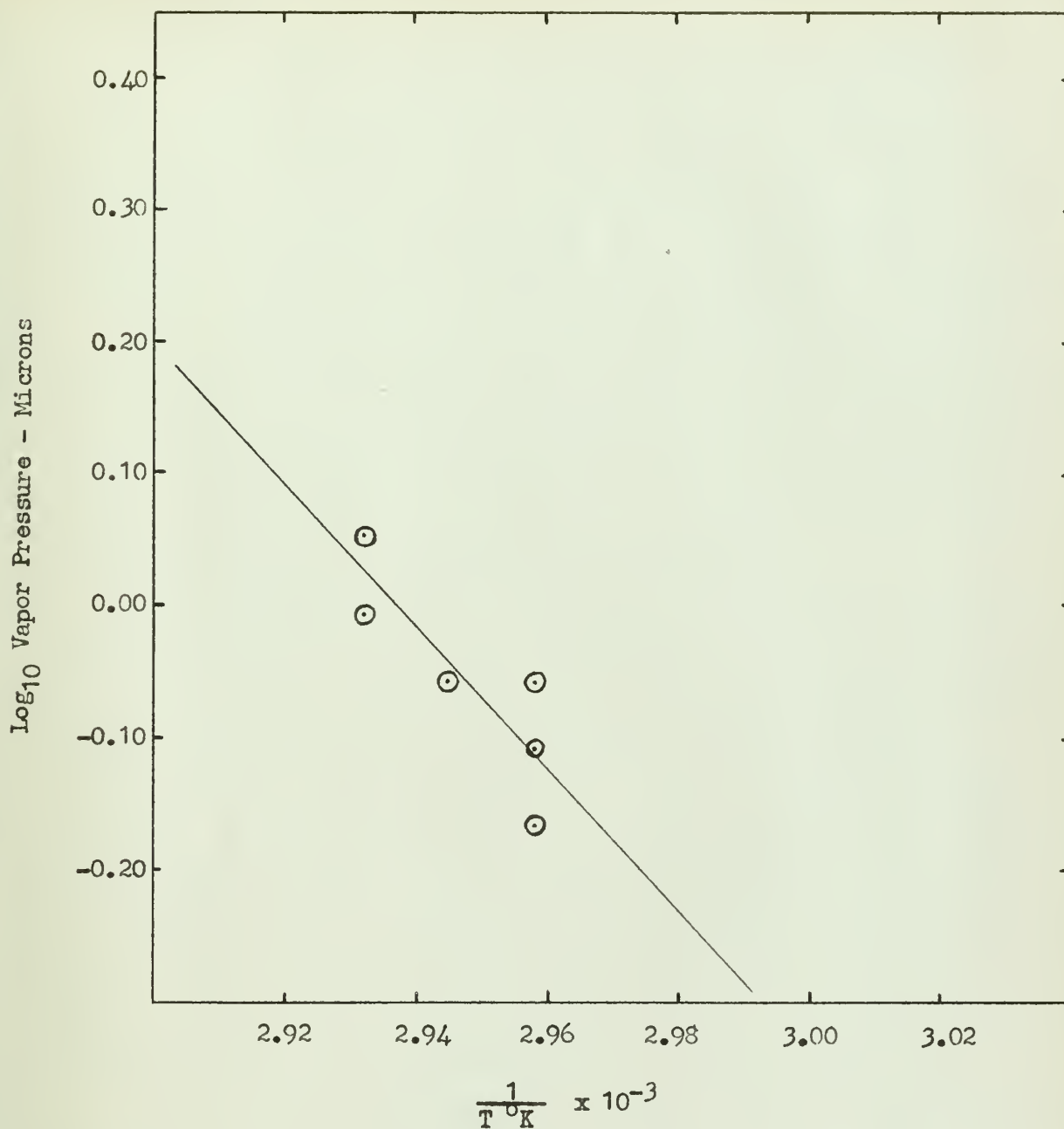


Figure 6. 2,4,6 - Trinitroanisole

7. Discussion.

The experiment on trinitrotoluene indicates that the equipment is capable of producing satisfactory results within its design range. By refining the technique, to increase the accuracy, a high degree of reliability is possible. This is significant when the simplicity of the equipment as compared to that used by other investigators is considered.

This simplicity has led to a number of limitations. As designed, the equipment cannot be used at temperatures above 80° C without changing the thermostat. For higher temperatures oil could replace water in the bath. Another technique would be to heat the base of the flask electrically and measure the temperature with thermocouples.

The second serious limit in the design is the vacuum to which the system may be run. The data for TNT indicates that this was approximately four percent of the vapor pressure being determined. Ideally, it is desired that this value be negligible. If not, it must be accurately measured. An attempt was made at measuring this pressure, but the results are in doubt. Because of the location of the ionization gage, there is some suspicion that the pressure being measured was not the same as that in the space above the orifice. Placing the gage on the flask, however, would seriously reduce the advantages of the simple system.

The most satisfactory method of correcting this error seems to be by reaching as low a pressure as possible. This may require changing the pumping system.

The third error-producing limitation involves timing. Unless runs are unusually long to cause the error to become insignificant, the four to five minute delay between starting evacuation and reaching the final vacuum must



be considered. This point probably contributed the largest single error to the determinations. The obvious solution is to employ faster pumping speeds. This can be immediately accomplished by installing an activated carbon trap in the system close to the flask. Between runs the carbon is baked out by means of a heating coil. When the equipment is connected for a run, a flask of liquid air is brought up on the trap. The rapid absorption of gas by the carbon will aid considerably in achieving a high vacuum very rapidly.

The final point to be considered is the contamination of the connecting parts and the gage stems of the vacuum system by the test material. There is no doubt that this adds greatly to the difficulty encountered in achieving a high ultimate vacuum. Cleaning between runs is not a complete answer. Some method of condensing these vapors before they reach that part of the system is needed. However, any such addition would reduce the original advantage of simplicity.

In general, it can be stated, recognizing the limitations of the equipment and the lack of experience in the actual determination of vapor pressures, that the original objectives of the project have been accomplished. The method chosen and the equipment constructed are suitable for measuring the vapor pressure of organic crystals.

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APPENDIX I

MEAN FREE PATH DETERMINATION

The maximum linear dimension of the orifice used in this experiment is fixed by the mean free path of the substance at the conditions of the test. This quantity can be determined by the following equation:

$$L = \frac{1}{\sqrt{2} n s^2}$$

where L is the mean free path in centimeters, n the number of molecules per cubic centimeter of the gas, and s the molecular diameter in centimeters.

It is obvious from this expression that the mean free path is inversely proportional to the density of the gas. At constant volume and temperature, the density is directly proportional to pressure; therefore the mean free path is inversely proportional to pressure.

In order to calculate the mean free path of the molecules, at equilibrium in the box used in the experiment, the vapor pressure of the material must be known or estimated.

For the investigation of trinitroanisole, with no data on its vapor pressure available, an approximation can be made by noting that its structure and molecular weight are very similar to trinitrotoluene. The known vapor pressure of trinitrotoluene is then assumed for use in the equation.

The molecular size is easily approximated by construction and measurement of a Fischer-Taylor-Herschfelder atomic model.

As an example, using the vapor pressure of TNT at 60°C, 5×10^{-4} mm, and the molecular size, 10 Angstrom units, for an estimate, the length of

the mean free path of trinitroanisole at this temperature and pressure was found to be approximately 14 centimeters. The orifice sizes used in this experiment were much smaller than the maximum allowable limit.

APPENDIX II

PURIFICATION OF THE COMPOUNDS TO BE TESTED

The materials tested in this project were purified by a recrystallization technique. Acetone was used for both trinitrotoluene and trinitroanisole.

Commercially pure crystals of the explosive were dissolved in a small quantity of acetone by warming gently in a water bath. The liquid was filtered and then drowned in a large beaker of cold distilled water. When precipitation was complete, the water was decanted off and the solid transferred to a filter where it was washed with large quantities of water. After washing was complete and all excess water had been removed, the material was transferred to a Petri dish and placed in a vacuum oven to dry. A melting point determination was made after each recrystallization and the procedure repeated until a constant melting point was obtained. The pure material was thoroughly dried under vacuum and at a temperature just below the melting point until successive weighings were constant.

APPENDIX III

DETERMINATION OF THE ORIFICE SIZE

The area of the effusion orifice was measured by a microscopic technique as follows:

A photomicrograph of the hole was taken on a standard metallurgical camera. Without changing the magnification settings, a picture was taken of the stage micrometer normally used for determining magnification. This second picture was used to construct a standard grid.

The area of the orifice was then cut from the first picture and weighed. A standard grid was cut from the same paper and its weight compared to the unknown area.

The average of three separate samples was used as the area in the vapor pressure calculations. The small deviation between samples indicated that with care this technique is quite satisfactory.

APPENDIX IV

CLEANING AND OUTGASSING

The vacuum system requires cleaning before using and after each determination. A certain amount of the material lost in effusion will condense out on the walls of the flask and along the arm connecting the flask to the cold trap. The cold trap must also be cleaned whenever the equipment is shut down to prevent the vapors condensed in it from vaporizing and reentering the rest of the system. Outgassing must follow each cleaning to remove any traces of solvent and moisture which may be introduced in the cleaning. When not in use, the system should remain sealed from the atmosphere.

1. Flask and Base

These units are cleaned with solvent, preferably high purity alcohol, and baked in an oven at 200°C for a minimum of 30 minutes before each run. If possible, a vacuum oven should be used. However, if pure solvent is used in the cleaning the outgassing under vacuum does not seem to be necessary.

2. Cold Trap

The base of the trap is removed, cleaned with pure solvent and allowed to dry. All of the stopcock grease is removed and replaced. The core is cleaned with lint-free laboratory tissue, fastened to the end of a short rod. Stubborn deposits can be removed by wetting the tissue lightly with solvent. Changing of the tissue often is required for a thorough cleaning. This procedure is required only when the equipment is to be shut down. No outgassing is required of the cold trap.

3. Gage Stems, Connecting Arms

Between each run the section of the system connecting the flask to the cold trap and holding the gages must be cleaned of deposited material. This can be done by passing dry lint free tissues through the section. If solvent is required to clean stubborn deposits, then a longer outgassing period must be allowed. After this section has been cleaned the joint to which the flask is attached is closed off with a ground glass plug and the system evacuated. A strip of thermal tape wound around this section supplies the heat required for outgassing. It is recommended that outgassing continue until the flask is ready to connect to the system. Evacuation of the system for cleaning and outgassing is accomplished by use of an auxiliary pump. At no time other than during a run should the diffusion pump be opened to the system. The auxiliary pump is protected from possible condensable vapors by a small cold trap.

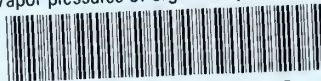
4. Stopcocks and Joints

Prior to starting up the system after a shutdown, all stopcocks and joints should be taken apart, cleaned, and fresh High Vacuum Silicone Grease applied. "O" rings should be inspected and replaced if necessary.

The precautions listed herein are absolutely necessary if the desired vacuum is to be attained.

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Vapor pressures of organic explosive com



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